

ATOMS AND MOLECULES

**An Introduction for Students
of Physical Chemistry**

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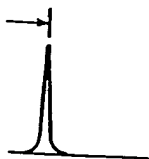
To
R. I. K., C. M. P.,
and their

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showing hyperfine interaction.

$$m, m_I \quad (7.197)$$

and has units of Hz. Equally, $\Delta m_I = \pm 1$, $\Delta m_I = 0$ are the frequencies of the

$$+\frac{1}{2} \quad (7.198a)$$

$$-\frac{1}{2} \quad (7.198b)$$

the hyperfine constant a . frequency by varying the

$$-\frac{1}{2} a \quad (7.199)$$

that lead to resonance.

$$\frac{ah}{2g\mu_B} = \frac{ah}{g\mu_B} \quad (7.200)$$

other atoms. If $\Delta\nu$ is have

$$9 \Delta\mathcal{B} \quad (7.201)$$

nts are quoted in both al making the measurement depends only on re exist methods (e.g.,

NMR chemical-shift measurements of systems with unpaired electrons) for determining the sign of a in appropriate cases.

For the hydrogen atom, the experimental value of a is 1420.4057 MHz or 506.84 G. Its source, already mentioned above, is the coupling between the nucleus and the electron magnetic moments. The quantitative expression for the hyperfine constant of a hydrogen atom expressed in Hz is

$$a = \frac{8\pi}{3h} g_e \mu_B g_H \mu_N |\psi(0)|^2 \quad (7.202)$$

where g_H and μ_N are the proton g factor and the nuclear magneton, respectively, and $|\psi(0)|^2$ represents the absolute value squared of the electron density at the nucleus. The coupling corresponding to Eq. 7.202 is often called the contact interaction, or *Fermi contact interaction*, after Enrico Fermi who showed (1930) that such an interaction should exist long before the ESR technique was introduced (1945-47). In addition to the Fermi contact term, there is another interaction between the electron and nuclear spins, which contributes for electrons in non- S states. This is the direct dipole-dipole term, which averages to zero in solution because of the rapid tumbling, but can be observed in solids when the molecules have fixed orientations.

From the form of the ground-state hydrogen-atom wave function (Section 3.2)

$$\psi_{1s} = (\pi a_0^3)^{-1/2} \exp\left(-\frac{r}{a_0}\right)$$

the electron density at the nucleus is

$$|\psi_{1s}(0)|^2 = \frac{1}{\pi a_0^3}$$

Substituting this result into Eq. 7.202 with the values for the various constants, we obtain 1422.75 MHz or 507.68 G, in reasonable agreement with experiment (see Problem 7.48). Correction for the finite mass of the proton [i.e., multiplication by $(1836.13/1837.13)^3$] gives the more accurate theoretical value 1420.43 MHz.

We consider now the extension of the hydrogen-atom results to more complex systems, in particular the organic radicals that are being intensively studied by ESR techniques. Such molecules contain many electrons, each of which has a spin and an associated magnetic moment. However, we can frequently neglect all of the inner-shell electrons, which form closed shells with paired spins, and restrict the discussion to the outermost electron with an unpaired spin that can interact with the external magnetic field. For the naphthalene negative ion (see Section 6.4.2), the ground-state